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Viscosity of liquid water from computer simulations with a polarizable potential model

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The longitudinal and shear viscosity of water are calculated by molecular dynamics simulation with a polarizable potential model at room temperature. To overcome the difficulty of evaluating directly the stress autocorrelation function of a system with intrinsically many-body forces, we have resorted to the analysis of the wave-vector-dependent longitudinal and transverse-current correlation functions. In a memory function formalism, the generalized viscosity can be evaluated as a function of the wave vector k. By extrapolating to $k=0$, we find longitudinal and shear viscosity values in better agreement with the experimental value than the corresponding quantities evaluated by making use of a nonpolarizable potential model. This result points out that for a realistic reproduction of transport quantities, it is crucial to take into account many-body contributions to the interaction potential.

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Due to its relevance in any physical process, water has widely been investigated both experimentally and by computer simulations. Several potential models have been proposed to simulate this important system and quite recently it has been demonstrated that many-body effects introduced by accounting for the molecular polarizability improve considerably the realism by which the properties of the liquid can be reproduced. The models implemented by Brodholt, Sampoli, and Vallauri [1] (henceforth referred to as BSV model) and Kusalik, Liden, and Svishchev [2] are found to account quite well for the temperature dependence of the density, giving its maximum at the right value of 278 K [3]. Moreover, the structure set up by the BSV model turns out to be well representative of the real structure of the liquid over a wide range of temperatures and pressures [4,5]. Not much is known of how the model is able to reproduce the transport coefficients of the real system, apart from the diffusion coefficient, evaluated both from the center-of-mass mean-square displacement [1] and velocity autocorrelation function [6], which was found in good agreement with the experimental finding at room temperature. Nonpolarizable models, such as the well-known transferable interaction potential four point (TIP4P) [7] and simple point charge extended models [8], fail instead to reproduce both the diffusion and shear viscosity coefficients [9,10].

The evaluation of the shear viscosity η through the standard Green-Kubo expression [11]

$$\eta=\frac{1}{VK_BT}\int_0^\infty\langle\sigma^{xy}(0)\sigma^{xy}(t)\rangle dt \tag{1}$$

is far from trivial when a polarizable model is used. In Eq. (1), $\sigma^{xy}(t)$ is one of the off-diagonal components of the stress tensor:

$$\sigma^{xy}(t)=\sum_{i=1}^{N} m_i v_i^x v_i^y-\tfrac{1}{2}\sum_{i\neq j}^{N} x_{ij}F_{ij}^y, \tag{2}$$

where v_i^x represents the x component of the center-of-mass velocity $\mathbf{v}_i$ x_{ij} the x component of the relative separation of particles i and j, and $\mathbf{F}_{ij}$ the force between them. As a matter of fact, expression (2), which is the molecular definition of the stress tensor, with all the quantities referred to the molecular center of mass, cannot be used for polarizable potential models, since the forces between molecules are not pairwise additive. The forces resulting from the induced dipoles depend in fact on the positions of all the molecules of the system.

An alternative route to the evaluation of η goes through the calculation of the wave-vector-dependent transverse-current correlation function

$$C_T(k,t)=\frac{1}{N}\langle j_x^*(k,0)j_x(k,t)\rangle, \tag{3}$$

where

$$j_x(k,t)=\sum_{i=1}^{N} v_i^x(t)\exp[ikz_i(t)] \tag{4}$$

is the transverse current, having set the wave vector $\mathbf{k}$ parallel to the z axis.

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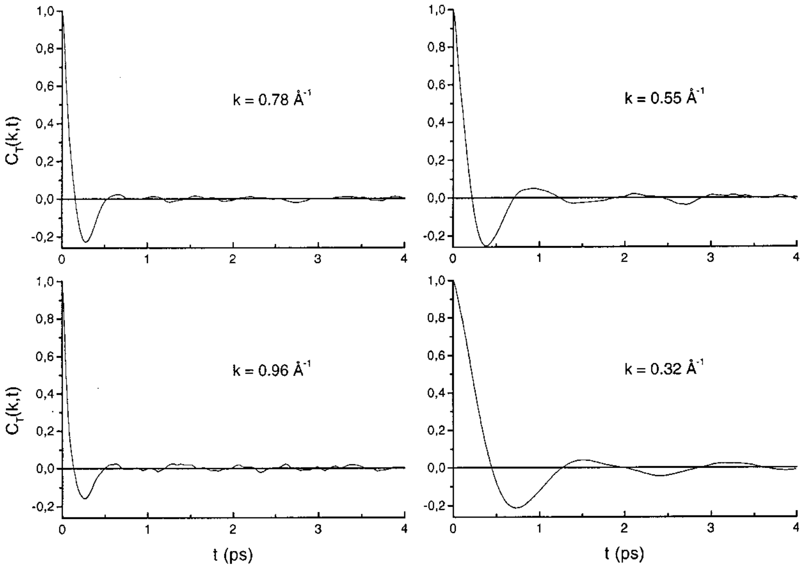

FIG. 1. Transverse-current correlation functions at four wave vectors for liquid water at $T=298\,\mathrm{K}$, using the BSV polarizable potential model, normalized to their initial value.

As is well known in the hydrodynamic ($k\rightarrow 0$) limit, C_T turns out to be

$$C_T(k\rightarrow 0,t)=\frac{K_BT}{m}\exp\left(-k^2\frac{\eta}{\rho}|t|\right), \tag{5}$$

where ρ is the mass density. In the Mori-Zwanzig projection formalism one can define a generalized viscosity proportional to the memory function of $C_T(k,t)$,

$$M_T(k,t)=\frac{k^2}{\rho}\,\eta(k,t), \tag{6}$$

such that the Laplace transform of $C_T(k,t)$, $\Psi_T(k,z)$ reads

$$\Psi_T(k,z)=\frac{K_BT/m}{z+M_T(k,z)}=\frac{K_BT/m}{z+(k^2/\rho)\,\eta(k,z)}. \tag{7}$$

From Eq. (7) one easily derives

$$\eta(k,z=0)=\frac{\rho}{k^2}\,\frac{(K_BT/m)}{\Psi_T(k,z=0)}. \tag{8}$$

As $\Psi_T(k,z=0)/(K_BT/m)$ is the area under the normalized transverse-current correlation function, a wave-vector-dependent generalized viscosity can directly be derived from computer-simulation results of an easily obtainable quantity. The extrapolation to $k=0$ of expression (8) gives the hydrodynamic value of this generalized transport coefficient, namely, the usual shear viscosity η. In Ref. [12], such a procedure has been used to derive the shear viscosity of Lennard-Jones, CO_2, and TIP4P water systems.

After having generated a trajectory of 40 ps in phase space using the BSV potential model with 256 molecules [13], we have evaluated the transverse-current correlation function $C_T(k,t)$ for a large set of k values chosen of the form $(2\pi/L)(n_1,n_2,n_3)$ with $n_{1,2,3}$ integers. To improve the statistics, all the combinations of (n_1,n_2,n_3) that lead to the same value of k were used. It turns out that at the smallest wave vector accessible to the present simulation, $k_{\mathrm{min}}=0.32\,\text{Å}^{-1}$, $C_T(k,t)$ becomes negative, thus indicating that we are outside the hydrodynamic regime. As already noticed, the system is in fact able to sustain shear waves at this wave vector [13]. For the sake of completeness, we report in Fig. 1 the behavior of $C_T(k,t)$ at four selected wave vectors.

In order to obtain a value for η by an extrapolation of the results for $\eta(k)$ at $k=0$, we have first followed the procedure indicated in Ref. [12]. We have approximated $\eta(k)$ at small k as

$$\eta(k)=\eta(1-\alpha k^2) \tag{9}$$

and varied the number of k values over which to perform the fitting of the two parameters η and α. We find that for $k<1.12\,\text{Å}^{-1}$, the result of the fitting is independent of the number of points. The results of this calculation are shown in Fig. 2 where the dashed line represents the k dependence of $\eta(k)$, the symbols represent the molecular dynamics (MD) data, and the full curves represent the upper and lower limiting values of $\eta(k)$. The corresponding values of η turn out to be between 8.02 and 8.67 mP with an average value of

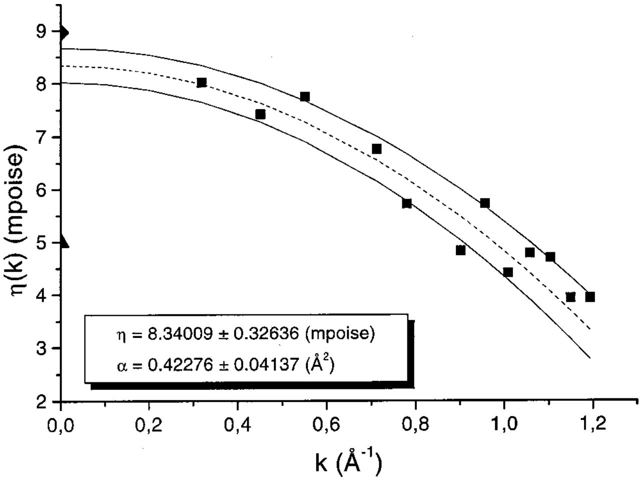

FIG. 2. Results of the fitting procedure to obtain η. Squares: MD data. Dashed line: $\eta(k)$ with the best-fitted values reported in the inset. Full lines: upper and lower values of $\eta(k)$ according to the uncertainty of η and α. The upper and lower symbols at $k=0$ represent the experimental and TIP4P values of η, respectively.

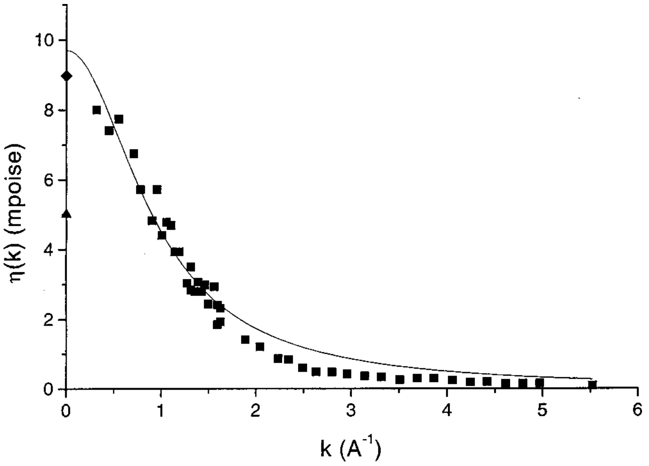

FIG. 3. Results of the fitting with expression (10) (full curve) of the MD data (squares). The symbols represent the experimental and TIP4P values of η, as in Fig. 2.

8.34 mP in fairly good agreement with the experimental value of 8.97 mP, obtained by extrapolating the experimental values of Ref. [14].

An extrapolation of approximation (9) to larger k values can be obtained by fitting the simulation data with an expression proposed to analyze the results for a dense hard-sphere system, at not too large wave vectors [15], i.e.,

$$\eta(k)=\frac{\eta}{1+a^2k^2}. \quad (10)$$

In Ref. [15] the best-fitted value of the parameter a turns out to be 0.3σ, where σ is the hard-sphere diameter. We have adopted a similar procedure by fitting Eq. (10) to the MD values of $\eta(k)$ obtained in the case of polarizable water. (See Fig. 3.) The fit yields $\eta=9.71\,\text{mP}$, which compares favorably with the value deduced from the experimental data. Remarkably enough, the best-fitted value of a turns out to be 0.32σ ($\sigma=3.2$ Å being the oxygen Lennard-Jones parameter), quite close to the hard-sphere result.

In contrast, recent calculations of the stress autocorrelation function of water at room temperature [9] have shown that for the TIP4P model, the resulting viscosity coefficient is 5.0 mP, nearly half of the experimental one. It is worth noticing that such a value is consistent with the one (4.49 mP) derived in Ref. [12] by adopting the same procedure used in the present paper, i.e., by extrapolating at $k=0$ the MD data for $\eta(k)$.

It is interesting to ascertain whether the improved agreement observed for the shear viscosity holds even for the other collective transport coefficients. To this aim, we have evaluated the *longitudinal* viscosity η_L with our available MD results for the longitudinal spectra $C_L(k,\omega)$ (see Ref. [13]), by the following procedure. In a simple viscoelastic approximation, the peak frequency ω_p of $C_L(k,\omega)$ turns out to be related to the relaxation time τ_k through the relation [11]

$$2(\omega_p^2)^2[\omega_P^2-\omega_L^2(k)]+\left(\frac{1}{\tau_k}\right)^2[(\omega_p^2)^2-\langle\omega_k^2\rangle^2]=0, \quad (11)$$

where $\langle\omega_k^2\rangle$ and $\omega_L^2(k)$ denote the second-frequency moments of the dynamic structure factor and of $C_L(k,\omega)$, respectively. The generalized longitudinal viscosity $\eta_L(k)$ follows from

$$\eta_L(k)=\frac{\rho}{k^2}[\omega_L^2(k)-\langle\omega_k^2\rangle]\tau_k. \quad (12)$$

Extrapolating to $k\to 0$, one obtains $\eta_L\approx 23\,\text{mP}$, still lower than the experimental value $\approx$30 mP, but better than the value obtained by MD simulation with a nonpolarizable potential model ($\approx$20 mP) [9]. Even if in this case the improvement is not so marked as for the shear viscosity (and somehow model dependent), this result stresses the positive outcome of considering polarization effects.

We conclude that many-body terms in the interaction potential are of crucial importance for a realistic representation of the properties of water. Having already shown that the structural and thermodynamic quantities [1,3,4,5] are well reproduced using the polarizable potential, the present and previous studies [1,13] confirm that even the transport coefficients are in better agreement with the experimental findings than those obtained by nonpolarizable potential models. Therefore, it is tempting to affirm that the BSV potential model is sufficiently realistic to derive both static and dynamical properties of water.

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